SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

CRF NEWS

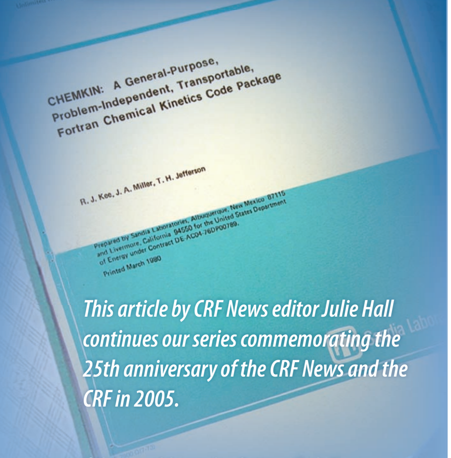
Celebrating 25 Years 1979–2004

COMBUSTION RESEARCH FACILITY

September/October 2004 • VOL. 26, NO. 5

CHEMKIN at 25

Chemical Kinetics Software is One of the CRF's Major Achievements


CHEMKIN: A General-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package

R. J. Kee, J. A. Miller, T. H. Jefferson

This article by CRF News editor Julie Hall continues our series commemorating the 25th anniversary of the CRF News and the CRF in 2005.

If they could turn back time, Bob Kee and Jim Miller would publish a paper on CHEMKIN in a scientific journal. Both were so caught up in refining and using CHEMKIN as a tool that once the SAND report (a type of Sandia publication) was published, they focused on publishing research results using CHEMKIN.

Had a journal article been published, "it would have been one of the most cited papers in the combustion literature," Kee said, adding that CHEMKIN was simply regarded as "a tool that facilitated what we really cared about"—the chemistry of flames.

CHEMKIN's usefulness as a tool for incorporating complex chemical kinetics into simulations of reacting flow is known the world over in the scientific and engineering community. It is the de facto standard for modeling of gas- and surface-phase chemistry and is used in the microelectronics, combustion, and chemical processing industries. Using CHEMKIN, researchers are able to investigate thousands of reaction combinations to develop a comprehensive understanding of a

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Sandia National Laboratories

Natural Gas Imager Performs Well in Japan Demonstration

CRF researchers successfully demonstrated a natural gas (methane) imaging system in February at the facilities of the Tokyo and Osaka Gas Companies, capping a four-year development effort at Sandia funded by the Japan Gas Association (JGA) and managed by the Gas Technology Institute (GTI) in the U.S. The work was part of the "National Project Against Natural Gas Leaks" initiated by the Japanese Ministry of Economy, Trade, and Industry (METI) to streamline mandatory leak detection processes performed by Japanese utilties. are collected at each pixel, and the logarithm of their ratio is displayed. This differential operation removes all scene elements except the gas plume from the image, making it easier for the operator to see the leak.

Figure 1 shows the imager schematic. Infrared radiation at 3270.4 nm is produced by an optical parametric generator (OPG) consisting of a crystal of periodically poled lithium niobate (PPLN). The OPG is pumped by a Sandia-developed Nd:YAG microlaser and seeded by a diode laser emitting at 1577.3 nm. The

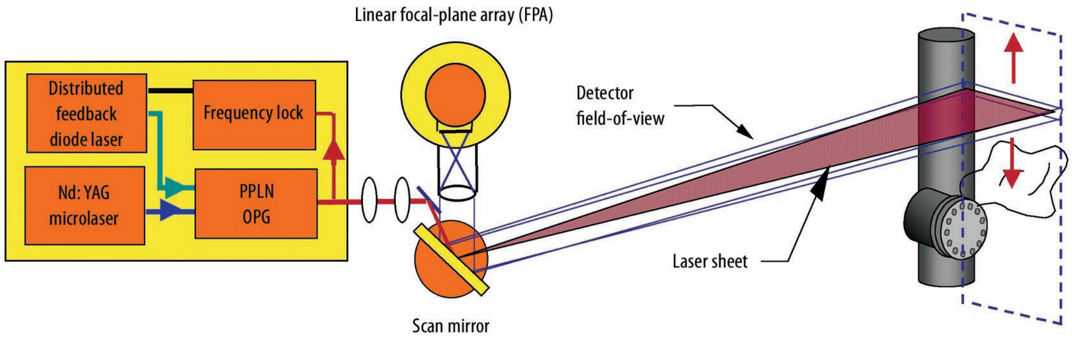


Figure 1. Diagram of the operation of the methane imager. The 3.3 μm light used for illumination is generated by the diode-seeded periodically poled lithium niobate (PPLN) optical parametric generator (OPG). It is formed into a line of light to illuminate the field-of-view of a linear focal-plane detector array. The laser and field-of-view are scanned vertically by a scan mirror.

While the methane imager operates according to the same principle as earlier imagers developed at the CRF for sensing hydrocarbons at petroleum refineries, it employs significant advances. All imagers use infrared (IR) laser radiation to illuminate a scene while it is viewed through an IR camera. Gases present that absorb the laser light produce a dark cloud in the video image. Whereas past devices used only one wavelength, the methane imager can illuminate at two: one absorbed by the gas of interest (the "on" wavelength) and one not absorbed (the "off" wavelength). When two wavelengths are used, the on and off signals

IR wavelength corresponds to the difference between the microlaser and diode wavelengths. The imager tunes the diode to maintain overlap of the output with the methane absorption, as well as to perform on/off wavelength switching. The laser emits pairs of pulses at a rate of 1818 Hz; they are formatted to illuminate a line in the scene. The illuminated line is viewed by a detector array, and both the line illumination and the detector field-of-view are swept up and down by a scan mirror to make an image.

The tests in Japan were conducted at the Tokyo and Osaka Gas Safety Schools, where gas

(Continued on page 5)

CHEMKIN *(Continued from page 1)*

particular process, which typically involves multiple chemical species, concentration ranges, and gas temperatures.

It also is viewed by many to be one of the most successful and enduring products to come out of Sandia National Laboratories. CHEMKIN is probably the CRF's most visible and far-reaching accomplishment, according to University of Utah professor and former CRF Advisory Board member Adel Sarofim. "CHEMKIN has been the product of the CRF that has found the greatest application among the combustion community, providing the CRF with high visibility and good will."

Now managed and distributed exclusively by San Diego-based Reaction Design, CHEMKIN is licensed to about 350 institutions worldwide. Because some organizations have multiple sites and multiple users, the total number of users is difficult to judge, according to John Garrison, vice president of sales and marketing for Reaction Design. In addition, the company offers computational fluid dynamics plug-in products that have incorporated the underlying CHEMKIN engine. A number of scientists still use older versions of CHEMKIN they obtained when Sandia was handling distribution, making it even more difficult to determine the actual number of users.

Reaction Design recently released CHEMKIN 4.0, which has a new user interface that "allows users to easily build more complex models of reacting flow and creates a simulation environment that is intuitive, including context-sensitive help and documentation," according to the company's Web site. The interface is a far cry from CHEMKIN's early days as a collection of Fortran source code distributed on magnetic tapes.

Born out of necessity

In the mid-1970s, Sandia mechanical engineer Bob Kee began working with physical chemist Jim Miller on combustion modeling, about the same time the Combustion Research Facility was in the proposal stages. They were particularly interested in how elementary chemical kinetics affected the structure of hydrogen-air diffusion flames. Kee, whose job was to implement these models in software, was frustrated by his observation that chemists "could never make their minds up about reactions mechanisms and were changing them several times a day."

"That became really burdensome when you're writing software," he said. "Plainly, what had to be done was to get more efficiencies in what we were doing."

Kee and Miller recognized that they needed to handle increasingly complex chemistry and transport phenomena in a general way, independent of the type of flame. They also needed to increase their efficiencies in developing new models for different combustion situations. They recognized that they could isolate the solution techniques from physical models, thereby benefiting from the rapid advancements in computational mathematics and software.

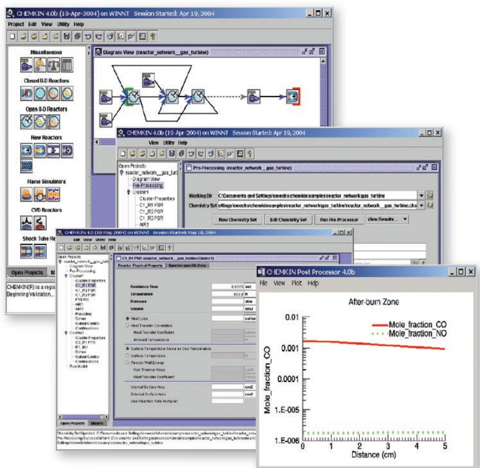
Kee's idea was to compartmentalize the code into hundreds of task-specific subroutines, only a few of which are needed for any particular program.

"The real genius. . . was in recognizing there would be a lot of applications and in taking these common routines and putting them off in a 'library' that would be used over and over," said Sandian Andy Lutz, who played a major role in writing a CHEMKIN application called SENKIN in 1987.

Miller, who calls himself the "consulting architect," had specific problems he wanted to solve in certain ways and provided guidance on CHEMKIN's design to achieve this. Applied mathematician Tom Jefferson and programmer Donna Mitchell were also involved in the beginning.

CHEMKIN's early days

In 1980, Sandia published the CHEMKIN manual for unlimited distribution. By this time, the CRF was beginning operation, and combustion researchers were traveling to



Examples of CHEMKIN 4.0's user interface.

Livermore. Kee and the others began to share the software with visitors who were interested in using CHEMKIN in their research. Initially, the Department of Energy restricted distribution to collaborators and visitors. Kee said that as CHEMKIN became more widely known, the definition of a CRF collaborator or visitor became blurred to such an extent that a telephone call was often sufficient.

"By the mid-1980s, we were clearly in the software distribution business, and the software was having noticeable impact on combustion research," he wrote in notes for a 1998 presentation.

The original CHEMKIN team had expanded by three, with the hiring of Mitch Smooke, Linda Petzold, and later Joe Grcar, as the team recognized the need to increase the sophistication of numerical solution techniques. Kee recruited secretary Fran Rupley to assist as the support needs grew along with the distribution, and she became a programmer a couple of years later through a Sandia mentoring and education program. Rupley, who retired from Sandia in 1999, currently works for Reaction Design.

While CHEMKIN initially dealt with chemistry alone, its developers knew it would have to incorporate interactions between fluid mechanics and chemical kinetic to be useful in modeling a flame. In the early 1980s, Juergen Warnatz, a longtime CRF collaborator, was writing code for this at the University of Heidelberg. Kee collaborated with Warnatz and Graham Dixon-Lewis at the University of Leeds to develop a molecular transport library that was compatible with the CHEMKIN architecture.

By the late 1980s, the interests of the group were moving increasingly to materials processing using chemical vapor deposition techniques. The shift prompted the development of major new capabilities within the CHEMKIN framework. Mike Coltrin, a physical chemist at Sandia's New Mexico site known for pioneering research in the development of detailed models of chemical vapor deposition, spearheaded the development of Surface CHEMKIN to deal with elementary heterogeneous chemistry at deposition surfaces. Later, Sandian Ellen Meeks, now a Reaction Design vice president, began working on plasma processes, which were incorporated into CHEMKIN.

By the mid-1990s, more than 1,000 copies of CHEMKIN had been distributed to the international research community. The software was a mix of old and new code, often customized by researchers for their own purposes. Sandia's support costs were growing steadily. In 1995, Sandia decided to license CHEMKIN for a fee in accordance with DOE policies at the time.

At about the same time, David Klipstein, who had already founded and sold one company, was establishing a new company to focus on the application of chemical kinetics and reaction simulation to a range of industrial chemistry problems. In 1997, Sandia licensed CHEMKIN to Reaction Design, founded by Klipstein and Massachusetts Institute of Technology professor Greg McRae, currently a CRF Advisory Board member.

Kee retired from Sandia in 1996 and is now a chaired professor at the Colorado School of Mines. His research group is currently writing software based on CHEMKIN to deal with charge transfer reactions and electrochemistry—important for the development of fuel cells.

CHEMKIN's future

Working with Sandia, Reaction Design continues to enhance the capabilities and usability of CHEMKIN while also providing technical support. Reaction Design and Sandia sponsor biennial workshops for existing and potential users. These workshops provide opportunities for exchanging ideas and exploring new directions in the application and advancement of CHEMKIN. The fourth such workshop was held July 25 in Chicago, prior to the International Symposium on Combustion.

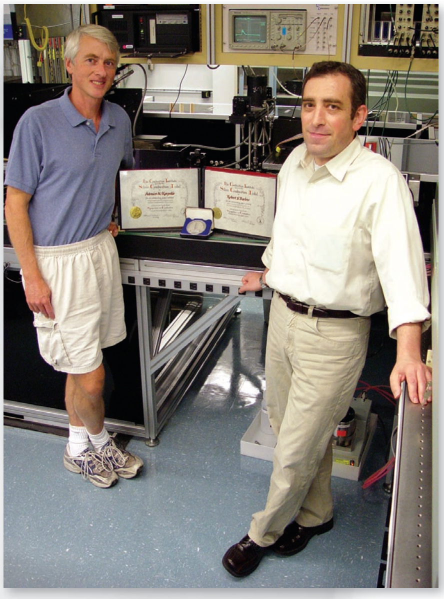
Taatjes Awarded JILA Fellowship

Sandia chemist Craig Taatjes has been awarded a five-month visiting fellowship starting in September at JILA in Boulder, Colo. Taatjes plans to work with JILA fellows Jun Ye, Dana Anderson, and David Nesbitt on sensitive spectroscopy of cold molecules, Bose-Einstein condensates on a chip, and single molecule microscopy and kinetics.

Since its founding in 1962, JILA has offered visiting fellowship appointments to distinguished scientists from all over the world. The competitive program allows recipients, working with resident scientists, to engage in research in areas of interest to JILA.

JILA (formerly known as the Joint Institute for Laboratory Astrophysics) is jointly operated by the University of Colorado and the National Institute of Standards and Technology.

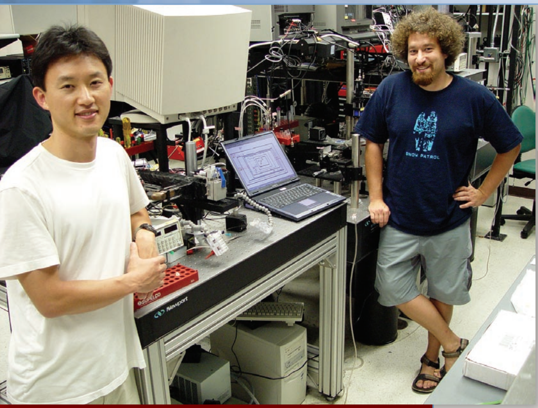
CRF Researchers Receive Combustion Institute Silver Medal for Paper



The Combustion Institute awarded the silver medal to Rob Barlow (left) and postdoc Adonios Karpetis (right) for "an outstanding paper presented at the "Twenty-Ninth Symposium on Combustion 2002." Their paper, "Measurements of Scalar Dissipation in a Turbulent Piloted Methane/Air Jet Flame," was selected from more than 350 papers. The award was presented July 29 at the 30th symposium in Chicago. Barlow, a principal member of Sandia's technical staff, was a major presence at the meeting as a proceedings editor, coauthor of one of the plenary lectures celebrating the 30th symposium and 50th anniversary of the Combustion Institute, coauthor with Karpetis on two contributed papers, and organizer of the Workshop on Turbulent Non-Premixed Flames that precedes the symposium. His work on turbulent combustion was frequently referenced in the presentations as benchmarks for the combustion community. Karpetis will complete his postdoc appointment this fall and then take a faculty position in aerospace engineering at Texas A&M University.

Sandia postdoc Blanca Lapizco-Encinas (left) has taken a professor position in the Chemical Engineering Department at the Universidad Autónoma de Nuevo León, in Nuevo León, Mexico. For more than a year, Lapizco-Encinas had been working with Yolanda Fintschenko (right) and others in the Microfluidics and Separations Department on insulator-based dielectrophoresis for the selective concentration and separation of live bacteria in water (see *CRF News*, November/December 2003). The work was featured on the March cover of *Analytical Chemistry* and also published in the June issue of *Electrophoresis* (v. 25, no. 10-11, pages 1695-1704).

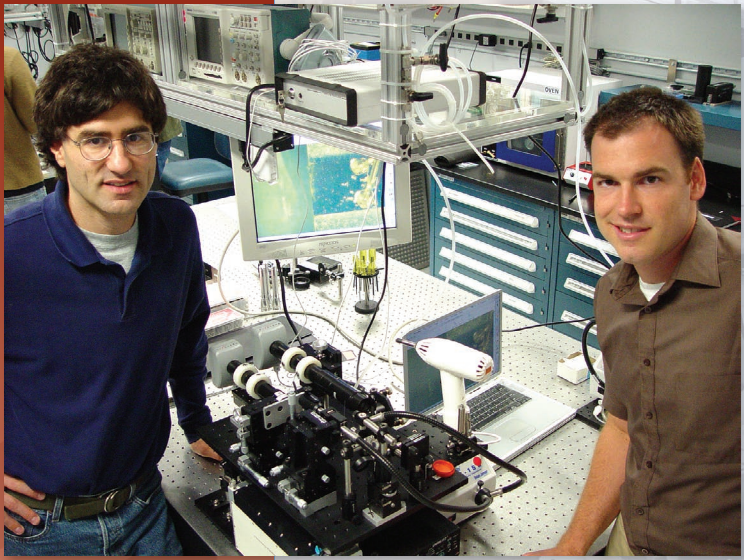
James Sutherland left the CRF in July for a postdoctoral fellowship in the Thermal/Fluid Computational Engineering Sciences Department at Sandia's New Mexico site. Sutherland, a Ph.D. student with Professor Phil Smith at the University of Utah, conducted his thesis research in residence at the CRF under the mentorship of Sandian Jackie Chen. He had worked with her since August 2001 on evaluating combustion models using direct numerical simulation.



Postdoc Simon Song (left) has accepted a faculty position in the Mechanical Engineering Department of Hanyang University in Seoul, Korea. For about the past two years, he has been working with Brian Kirby (right) in the Microfluidics Department on the development of microfluidic chips for bio-sample analysis using laser-patterned nanoporous polymer membranes. Kirby, a technical staff member at the CRF for more than three years, is also leaving the CRF to take an assistant professor position in the Sibley School of Mechanical and Aerospace Engineering at Cornell University.

2004 Summer Interns

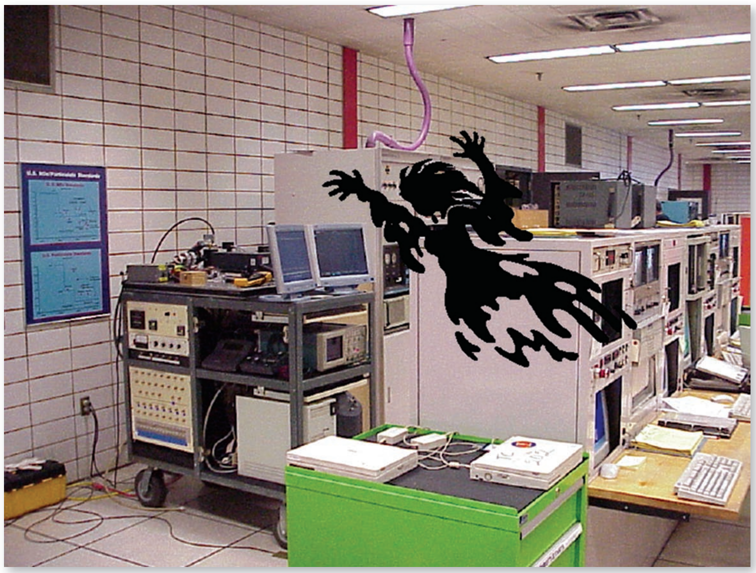
CRF summer interns work under the guidance of a mentor on a broad range of projects, both administrative and technical, ranging from Web site development to modeling in-cylinder diesel processes. Some of the students have spent several summers at the CRF. Front row (left to right): Chris Behrens (standing), University of California, Los Angeles; Tyrone Hill, Massachusetts Institute of Technology (MIT); Julianna Moats, University of California, Davis; Kendall Trudeau, California State University, Hayward; Kelsey Nyholm, Brigham Young University (BYU); Andrew Madewell, University of Arizona. Middle row: Kim LeBlanc, Clark University; Brent Pickett, BYU; Bryan Chu, Princeton University. Back row: Alicia Hardy, MIT; Mark Wiley, University of California, Santa Barbara; Brian Peterson, University of Michigan; Matthew Runyon, Tracy High School.



Kevin Aptowicz (right), a Yale University graduate student under applied physics professor Richard Chang, visited the CRF for three days in June to work with Dahv Kliner (left). Aptowicz has been awarded a Yale University Excellence in Engineering Fellowship (funded by Sandia National Laboratories) to collaborate with Kliner on real-time optical detection of biological aerosols.

Autonomous Diesel Particulate Measurements Show Value of Laser-Induced Incandescence

Federal diesel particulate matter (PM) emission regulations scheduled to take effect in 2007 pose two related challenges for the automotive industry: how to comply with the regulations and how to make reliable, low-level PM measurements during the engine and aftertreatment development process to demonstrate compliance. While laser-induced incandescence (LII) offers the potential for onboard, "real-world" PM measurements, it has been slow to gain acceptance because of presumed complexity of use and upfront costs (~$150,000 per instrument).



Sandia LII system at Cummins test facilities with unidentified (and unnecessary) operator.

CRF engineer Pete Witze has been collaborating with Greg Smallwood of the National Research Council, Canada, and Will Bachalo of Artium Technologies, Inc., to develop an LII instrument that could be subsequently commercialized (see *CRF News*, March/April 2004).

Witze has now shown that the LII instrument can be operated autonomously and continuously for extended periods of time. With the need for an around-the-clock operator eliminated, capital costs can be offset by labor cost savings. Witze presented a paper on the experiment in July at the Sixth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA) in Yokohama, Japan.

The experiment was conducted last fall at the Cummins Technical Center engine test facilities in Columbus, Ind., where they have five constant volume sampling (CVS) dilution systems. Each of three of the CVS systems is connected to two engine test cells, permitting testing of one engine while the other is being modified or swapped out. The remaining two CVS systems are tied to individual test cells. Cummins runs all four systems 24/7, with the assistance of operators to install and remove the PM sample filters used for the Environmental Protection Agency gravimetric measurement procedure.

Hosted by Shirish Shimpi and assisted by Russ Durrett and Bret Rankin of Cummins, Witze set up his LII system to run continuously and unattended, with the LII output signal connected directly to the Cummins data acquisition system. The equipment operated continuously in this mode for 7.5 weeks except for one inadvertent power disconnection (the system was brought back online within minutes once the interruption was discovered), logging 1,078 individual diesel engine tests.

The LII system recorded response to the elemental carbon portion of the diluted diesel PM exhaust sample; other sample components, such as semi-volatile organics and sulfates, were not detected by this technique. Witze is currently working on other techniques that would provide information on these other sample components.

The major issues regarding durability of the LII system are flashlamp lifetime and fouling of the windows in the optical cell. Witze estimates the flashlamp fired 60 million times during the test period, with no measurable deterioration in laser energy. A replacement flashlamp costs about $160 and is easily installed. An active air purge kept the cell windows spotless during the entire test period.

The results were compiled in a technical paper coauthored by Witze, Shimpi, Durrett, and Lisa Farrell, with data set assistance from Rich Wagner and Venkatesh Gopalkrishnan, all of Cummins.

Natural Gas Imager

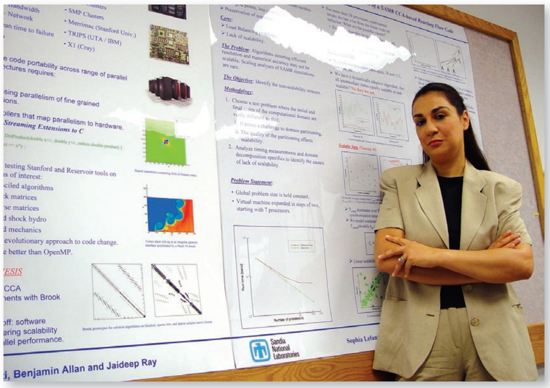
(Continued from page 1)

industry personnel are trained in gas safety. Hidden piping in the facilities creates synthetic "leaks" from floors, walls, and other locations. Industry representatives used the gas imager to detect these leaks, as well as other controlled emissions, verifying that it met their target range and sensitivity conditions and satisfying both the sponsors and gas industry participants.

Tom Reichardt and Kiran Kothari (of GTI) explain the operation of the JGA gas imager to attendees of the demo at the Tokyo Gas safety facility.

Lefantzi Selected for Program Honoring Top Young Engineers

CRF researcher Sophia Lefantzi was recently selected to participate in the 10th annual National Academy of Engineering's Frontiers of Engineering Symposium, a three-day event recognizing the nation's brightest young engineers. The 86 participants—from industry, academia, and government—were nominated by fellow engineers and chosen from more than 170 applicants.



Sophia Lefantzi

"I was thrilled and honored. I am looking forward to the symposium," said Lefantzi, who holds a master's degree in mechanical and aerospace engineering from Rutgers University.

Participants are engineers ages 30 to 45 who are performing cutting-edge engineering research and technical work in a variety of disciplines.

Lefantzi's selection was based on her work with the Computational Facility for Reacting Flow Science (CFRFS), a collaborative effort led by Sandia to advance the understanding and prediction of chemical reaction processes and their interactions with fluid flow (see **http://cfrfs.ca.sandia.gov**). CFRFS is funded by Scientific Discovery through Advanced Computing (SciDAC), a Department of Energy Office of Science program with the goal of achieving breakthrough scientific advances via computer simulation that are impossible using theoretical or laboratory studies alone.

Together with Habib Najm and Jaideep Ray, Lefantzi has been contributing to the development of software for high-performance combustion simulation utilizing a Common Component Architecture (CCA)-based toolkit for the simulation of time-evolving laboratory scale flames.

The symposium will be held Sept. 9-11 at the National Academies' Arnold and Mabel Beckman Center in Irvine, Calif., and will explore topics in multiscale modeling, designer materials, engineering for extreme environments, and engineering and entertainment.

CRF News Receives Award

The *CRF News* received an Award of Excellence in the Most Improved Newsletters category in Apex 2004, the sixteenth annual awards program recognizing excellence in publications work by professional communicators. The awards are based on excellence in graphic design, editorial content, and success in achieving overall communications effectiveness. *CRF News* launched its new design in the March 2004 25th anniversary issue.

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CRF News is a bimonthly publication of the Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551 0969. ISSN 1548-4300

Director .... William J. McLean
Editor .... Julie Hall
Graphic Artist .... Daniel Strong
Photography .... Daniel Strong

Subscriptions are free. Subscriptions and address changes to Julie Hall, jchall@sandia.gov.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC0494AL85000